(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 July 2001 (12.07.2001)

PCT

(10) International Publication Number
WO 01/49115 A1

(51) International Patent Classification[7]: A01N 25/34, 59/16, A61K 33/24, 33/38

(21) International Application Number: PCT/US01/00213

(22) International Filing Date: 4 January 2001 (04.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/477,883 5 January 2000 (05.01.2000) US
09/542,199 4 April 2000 (04.04.2000) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/49115 A1

(54) Title: HIGH PERFORMANCE SILVER (I, III) OXIDE AND COBALT (II, III) OXIDE ANTIMICROBIAL TEXTILE ARTICLES

(57) Abstract: Fibrous textile articles possessing enhanced antimicrobial properties are prepared by the deposition or interstitial precipitation of tetrasilver tetroxide (Ag_4O_4) or cobalt (II, III) oxide (Co_3O_4) crystals within the interstices of fibers, yarns, or fabrics forming such articles, as well as methods of preparing the same.

HIGH PERFORMANCE SILVER (I, III) OXIDE AND COBALT (II, III) OXIDE ANTIMICROBIAL TEXTILE ARTICLES

FIELD OF THE INVENTION

This invention relates to textile articles possessing antimicrobial properties and a method for their preparation.

DESCRIPTION OF RELATED ART

Chemical treatment of textile articles to render them microbicidal to microorganisms coming in contact with them is known in the art. Such articles include those made from paper, fibers, woven and non-woven textiles, and like fabrics which are designed for use in environments such as hospitals, food processing plants, laboratories, and other areas where maintenance of germ-free conditions is essential.

For example, U.S. Patent No. 2,791,518 to Stokes, Jr. et al. discloses a method of imparting microbicidal properties to articles such as textiles. The method recites to first immerse the article in a first aqueous solution containing a water-soluble basic nitrogen compound (*e.g.*, ammonia) and a monovalent silver salt, soluble in the solution, followed by a second immersion in a second solution containing a second salt, capable of ion exchange with the silver salt, such that a monovalent silver salt precipitate is formed within the article. The formed silver precipitate is sparingly water-soluble and imparts microbicidal properties to the articles so treated.

Similarly, U.S. Patent No. 5,271,952 to Liang et al. discloses a method of treating fibers to render them electrically conductive as well as anti-bacterial. The method includes immersing the fibers in a bath containing an aqueous solution of a source of divalent copper ions, a reducing agent, sodium thiosulfate, and a source of iodide ions, whereby copper iodide is adsorbed into the fibers. Similar techniques for rendering fibers conductive or resistant to bacteria involving the use of copper compounds are disclosed in U.S. Patent Nos. 4,410,593 to Tomibe et al. and 5,458,906 to Liang.

It has also been disclosed that materials such as chlorinated hydantions may be grafted to textiles for the purpose of imparting antimicrobial properties. *See, e.g.*, Williams et al., 218th ACS National Meeting (1999) Abstracts, Cell 32; C&EN September 6, page 36. Textiles so treated tend to suffer severe diminishment of antimicrobial properties after as few as 5 hours of laundering and are unstable after long durations of exposure to ultraviolet light.

One of the main problems associated with the use of monovalent silver

compounds, such as the halides, phosphates, or sulfates, in such applications is that they are sensitive to ultraviolet light and are thus prone to discoloration after exposure to sunlight, with a gradual loss of effectiveness of antimicrobial properties. Also, many of these compounds are soluble or slightly soluble in hot water which diminishes the antimicrobial properties after only a few launderings of reusable fabrics containing them.

Another problem with respect to the use of copper compounds as interstitially precipitated antimicrobials, described in U.S. Patent Nos. 5,271,952 and 5,458,906, is that these processes do not readily lend themselves to inclusion in textile production lines. Textile finishing lines involve processes which take minutes and cannot readily accommodate precipitations which require lengthy immersion times of sixty minutes or more.

The main object of the present invention is to provide a method of treating fibers and configurated textile products so that anti-microbial properties are imparted to them. Another object of the invention is to incorporate into the fibers and textile products powerful anti-microbial properties based on an electron active molecular crystal analogous to the molecular crystal, tetrasilver tetroxide, which has been proven to be one of the most powerful disinfectants known to man. Another object of the invention is to form a multivalent cobalt oxide by interstitial precipitation. Still another object of the invention is to enable rapid mass production of such anti-microbial fibers and textile products.

SUMMARY OF THE INVENTION

The invention relates to a fibrous textile article including a silver (I, III) or cobalt (II, III) oxide as an antimicrobial agent interstitially deposited within the article, the agent present in an amount sufficient to impart antimicrobial properties to the article. In the embodiment with cobalt (II, III) oxide, the article may also include a source of fluoride ions.

In one embodiment, the antimicrobial agent is interstitially deposited by interstitial precipitation. The article can include woven or non-woven fabric, or both.. In a preferred embodiment, the antimicrobial agent is present within the fabric at a level of about 0.5 to about 15,000 weight PPM, based on the weight of silver or cobalt. The antimicrobial properties are sufficient to yield microbial inhibition zones extending beyond 1 mm of fabric swatch borders as measured by AOAC test 972.04.

The invention further relates to a process for imparting antimicrobial properties to a fibrous textile article, including providing a first aqueous solution including a water-soluble silver or cobalt salt; contacting the article with the first aqueous solution for a period of time sufficient to uniformly wet the article with the first aqueous solution;

immersing the wetted article in a bath including a second aqueous solution including a strong alkali and a water soluble oxidizing agent and heating the bath for a period of time sufficient to interstitially precipitate tetrasilver tetroxide or cobalt (II, III) oxide with the article to yield a finished article; and removing the finished article from the bath.

In preferred embodiments, the silver salt includes silver nitrate or the cobalt salt includes cobalt chloride. The bath for the cobalt salt can further include a water-soluble fluoride salt, preferably at a concentration of about 10 to 1500 mg/L. In preferred embodiments, the alkali includes sodium hydroxide or potassium hydroxide and the oxidizing agent is sodium persulfate or potassium persulfate.

In one embodiment, the finished article includes about 0.5 to 15,000 PPM of the salt, based on the weight of the article. In preferred embodiments, the contact of the article with the first aqueous solution includes immersion of the article in the first aqueous solution for about 15 seconds to about 60 seconds and the time of immersion of the article in the second aqueous solution is about 30 seconds to about four minutes.

DETAILED DESCRIPTION OF THE INVENTION

Imparting antimicrobial properties to fiber and textile products is achieved in the instant invention by interstitial deposition of the molecular crystal compound tetrasilver tetroxide, *i.e.*, silver (I, III) oxide, or multivalent cobalt oxide, *i.e.*, cobalt (II, III) oxide. The silver moiety is the subject of several patents. U.S. Patent No. 5,336,499 to Antelman, the disclosure of which is incorporated herein by reference, describes the anti-pathogenic properties of silver oxide of formula Ag_4O_4 and also the mechanism of operation of the molecular device, based on a unique crystal having two monovalent silver (Ag I) ions and two trivalent silver (Ag III) ions in the molecule. It has now been found that cobalt (II, III) oxide (Co_30_4) is capable of killing pathogens in a like manner in textile articles.

U.S. Patent No. 5,211,855 to Antelman also discloses the use of Ag_4O_4 crystals to kill pathogens in utilitarian water bodies such as swimming pools.

An antimicrobial spectrum of Ag_4O_4 shown in Table 1 can be found in Antelman, "Silver (II, III) Disinfectants," *Soap Cosmetics Chemical Specialties* 1994, 70, 3 pp. 52-59. The spectrum is based on specifications of the Association of Official Analytical Chemists ("AOAC")

Table 1. Antimicrobial Spectrum of Ag_4O_4

MICROORGANISM	MIC* (ppm)
Gram Negatives	
Escherichia coli 10231	2.50
Escherichia coli 25254	2.50
Enterobacter cloacae 13047	1.25-2.50
Pseudomonas aeruginosa 9027	2.50
Gram Positives	
Bacillus subtilis 6633	1.25-2.50
Micrococcus lutena 9341	2.50-5.00
Staphylococcus aureus 0927	5.00
Staphylococcus aureus 27543	0.625
Staphylococcus epidermidis 12228	1.25-5.00
Streptococcus agalactiae 27956	5.00
Streptococcus faecium 10541	2.50
Streptococcus pyogenes 7958	5.00
Yeast and Mold	
Candida albicans 16404	2.50-5.0
Saccharomyces cerevisiae 2601	1.25

* minimal inhibitory concentration

Monovalent silver is more anti-pathogenic than mercury which is more anti-pathogenic than copper, based on their oligodynamic activity as articulated by J.G. Horsfal in "Principles of Fungicidal Action" (Chronica Botanica 1956). The relative efficacy of metallic moieties against pathogens has been called the Horsfal series:

$$Ag > Hg > Cu > Cd > Cr > Ni > Co > Zn > Fe > Ca$$

It has been found that with respect to a Horsfal series dedicated to silver, the relative efficacy against pathogens is as follows:

$$Ag_4O_4 > Ag(III) > Ag(II) > Ag(I)$$

The term "fibrous textile article" as used herein is intended to encompass a wide variety of materials including paper, natural or synthetic fibers, threads, and yarns made from materials such as cotton, rayon, wool, jute, nylon, polyesters, polyacetates, polyacrylics, as well as cellulosics in general. More particularly, the term refers to fibers

woven into a fabric such as knitting, and non-woven hydrophilic fabrics or webbing used in anti-pathogenic applications such as in the medical field, hospitals, biotechnology, and food and dairy processing. Examples of textile products in these fields include bandages, gauze, bandage pads, skin patches, work clothes (both disposable and reusable), bed sheets, masks, dust cloths, safety belts, surgical gowns, ambulance blankets, stretchers, filter materials, diapers, underwear, pajamas, video display terminal screens, and the like.

For some antimicrobial applications, a silver oxide or cobalt oxide, such as Ag_4O_4 or Co_3O_4 crystals, or both, may be deposited within the interstices of fibrous articles by simply soaking the article in an aqueous dispersion of the crystals (generally having a dimension of less than 100 angstroms), or by combining the crystals with a carrier medium and applying this composition to the fibrous article. This method of physical incorporation of the crystals is useful where the article is composed of low density or loosely associated fibers, such as bandage pads, gauze pads, and loosely non- woven products, and particularly laminated products wherein the treated fibrous article is subsequently sandwiched between one or two peelable layers which tend to keep the crystals trapped in the fibrous article until ready for use. Also, antimicrobial paper products may be made by simply mixing an aqueous dispersion of the oxide, such as Ag_4O_4 or Co_3O_4 crystals, or both, with paper pulp prior to calendaring the pulp.

Physical incorporation of the crystals may tend to be less effective, however, where the treated article is a fiber or yarn or a higher density woven or non-woven fabric, since the pre-formed crystals can not penetrate the interstices of such articles as easily. Deposition of the silver oxide or cobalt oxide material via interstitial precipitation is preferred in such cases.

Interstitial precipitation of the metal oxide crystals (generally having an average dimension of less than 100 angstroms) is accomplished by first providing an aqueous solution of, in the case of a silver oxide, a monovalent water-soluble silver salt such as the nitrate, perchlorate, acetate, methanesulfonate, or fluoride, most preferably silver nitrate. Next, the article to be treated, *e.g.*, a fiber or yarn of a woven or non-woven fabric, is thoroughly wetted with this solution such that the article absorbs the solution on fiber surfaces as well as one or more of the interstices between the fibrils forming the fiber, between fibers forming the yarn or non-woven fabric, or between the weft and woof yarns present in woven fabrics. Wetting may be accomplished by uniformly spraying the article, or more preferably by dipping the article in a bath of the silver or cobalt salt solution for a period of time sufficient for the article to absorb the requisite amount of silver or cobalt salt solution. This time may range from about 15 seconds to 60 seconds, more preferably about

30 seconds.

Next, the wetted article is removed from the immersion bath, optionally squeezed to remove excess solution, and immersed in a heated bath containing a second aqueous solution containing a strong alkali and a water soluble oxidizing agent, and heated for a period of time sufficient to cause reaction leading to the interstitial precipitation of tetrasilver tetroxide (Ag_4O_4) or Co_3O_4 crystal material in the interstices of the fibrous article. Suitable alkalis for this purpose include sodium or potassium hydroxide, with sodium hydroxide most preferred. Suitable oxidizing agents include alkali metal persulfates. Sodium, or more preferably potassium persulfate, is the preferred oxidizer. Reaction of the Ag_4O_4 in the bath is accomplished by heating at a temperature of at least about 85°C, more preferably at least about 90°C, for a period of time sufficient to maximize yield of Ag_4O_4, generally from about 30 seconds to about 5 minutes. Reaction for the Co_3O_4 in the bath is accomplished at room temperature.

After the reaction is completed, the treated article is removed from the bath and may be washed several times with water to remove soluble inpurities or unreacted reagant.

The quantity of Ag_4O_4 or Co_3O_4 material present in the resulting article will generally be a function of the quantity of silver or cobalt salt sorbed by the article, which can vary depending on the nature of the article, *e.g.*, loose vs. tight weave fabrics or whether the fiber is natural or synthetic, the former being more absorbant of the silver or cobalt salt solution.

For the tetrasilver tetroxide, in general, the quantity of alkali present in the second bath is preferably sufficient to maintain a strongly basic pH, *i.e.*, greater than about 13, and provide a slight molar excess of silver salt over oxidizing agent, suitable to complete the reaction. Thus, the content of tetrasilver tetroxide interstitially precipitated within any given fibrous article may be controlled by varying the concentration of the silver salt in the solution used to first wet the article and appropriately adjusting the quantities of alkali and oxidizing agent present in the immersion solution at approximately stoichiometric levels.

For the Co_3O_4, in general, the quantity of alkali present in the second bath should be sufficient to maintain a pH on the basic side, *i.e.*, above about 9. The content of Co_3O_4 crystals interstitially precipitated within any given fibrous article may be controlled by varying the concentration of the cobalt salt in the solution used to first wet the article.

The term "derivatives of Ag_4O_4" is intended to include Ag_4O_4 reaction products prepared by reacting Ag_4O_4 with suitable water-soluble acids to give the

corresponding Ag (II) salts, *e.g.*, reactions with fluoroboric acid or phosphoric acid to give the Ag (II) fluoroborate or phosphate, as disclosed in U.S. Patent No. 5,107,295 to Ibuhci. Divalent silver nitrate and divalent silver halides prepared by reacting Ag_4O_4 with nitric acid or the corresponding haloacids, *e.g.*, HBr, HI or HCl as disclosed in U.S. Patent No. 5,078,902 to Antelman are also included. Trivalent silver derivatives such as Ag (III) biguanide prepared in accordance with U.S. Patent No. 5,223,149 to Antelman are also included.

Textile articles containing such derivatives are prepared by further contacting the Ag_4O_4-containing article in an additional step with an aqueous solution containing up to stoichiometric amounts of the appropriate reagant(s) sufficient to convert at least a portion of the Ag_4O_4 to the Ag (II) or Ag (III) derivative.

The actual tetrasilver tetroxide is more preferred than textile articles containing such derivatives because some derivatives may be generally more water-soluble than Ag_4O_4, such that they can require a further processing step in their manufacture and can be less effective as antimicrobial agents than Ag_4O_4 as shown in the silver Horsfal series described above. Ag(II) or Ag(III) derivatives of Ag_4O_4 are, however, useful as antimicrobial agents in fabrics designed for a single use, such as bandages or disposable garments.

The content of the Ag_4O_4 or its derivatives (based on weight PPM silver) in the fabric may preferably range from as little as 0.5 weight PPM up to about 50,000 weight PPM, based on the weight of the textile article. The minimum content should be sufficient to kill pathogens from which protection is sought, whereas the maximum content is dictated by factors such as economy and affect on fabric properties. Generally, the higher the silver content, the more effective will be the antimicrobial properties of the article. Silver content in the range of from about 30 to about 10,000 weight PPM will provide satisfactory antimicrobial properties for most applications.

The antimicrobial properties of the articles treated with Co_3O_4 may be further enhanced by including a source of fluoride ions in the second oxidizing bath described above. Such sources include water-soluble fluoride salts, such as sodium or potassium fluoride. The amount of fluoride anion source may generally range from about 10 mg to 1500 mg per liter of solution, preferably from about 100 mg to 1000 mg per liter.

The content of the Co_3O_4 (based on weight PPM cobalt) in the fabric may range from as little as about 0.5 weight PPM up to about 15,000 weight PPM, based on the weight of the textile article. The minimum content should be sufficient to kill pathogens from which protection is sought, whereas the maximum content is dictated by factors such

as economy and affect on fabric properties. Generally, the higher the cobalt content, the more effective will be the antimicrobial properties of the fabric. Cobalt content from about 1000 weight PPM to about 15,000 weight PPM will provide satisfactory antimicrobial properties for most applications.

Antimicrobial properties are evaluated in accordance with this invention using the AOAC test method 972.04, which is used primarily to evaluate the bacteriostatic activity of laundry additive disinfectants. In this test, a square or rectangular sterile swatch of fabric is pressed into a petri dish containing a layer of nutrient agar that has been inoculated with a pathogen. Following a fixed period of incubation, each fabric sample is evaluated by measuring the clear zones adjacent the four sides of each test swatch as an index of antimicrobial activity. The presence of clear zones along all four sides of the swatch is indicative of antimicrobial activity, rated 4/4. The width of the clear zones in millimeters is reasonably indicative of the degree of antimicrobial activity.

EXAMPLES

The invention is further defined by reference to the following examples describing the invention in detail.

Example 1: A Nylon Article Prepared According to the Invention

A swatch of virgin nylon webbing was immersed in an aqueous solution containing dissolved silver nitrate at a concentration of about 100 PPM silver maintained at room temperature. After 30 seconds immersion time, the swatch was removed from this solution and immersed in a hot aqueous solution containing 7.2 g/liter each of NaOH and sodium persulfate. The solution was then boiled for one minute (95-100°C). The swatch was then removed from the boiling solution, washed with water, and dried.

A barely visible tan coating was observed on the swatch fibers. The content of Ag_4O_4 in the fabric swatch, measured as silver, was 89 weight PPM as verified by gravimetric analysis.

Examples 2-6: Nylon Articles Prepared According to the Invention

Example 1 was repeated, except that the concentration of silver nitrate in the first solution and reagents in the second solution were varied to provide the following Ag content in the fabric swatch:

	SOLUTION (PPM Ag)	FABRIC (PPM Ag)
Ex 2	890	35*
Ex 3	890	541
Ex 4	10,000	3970
Ex 5	10,000	9140
Ex 6	10,000	9140

*Nylon fabric for this test was of a tighter weave than that used in Example 1, which accounts for the lower silver absorption.

AOAC antipathogenic tests on these textiles were performed by an independent laboratory licensed by a State environmental regulatory body. The marker organisms used in conformity with AOAC test method 972.04 were Pseudemonas Aeroginosa (PA) as the Gram negative bacteria marker, and Staphylococcus Aureus (SA) for Gram positive bacteria.

The tests were conducted in terms of inhibition of cultures of the bacteria. Two swatches were used for the tests in contact with the cultures. The swatches were 1.5 inches wide and had a density of about 69 mg/cm^2. Each swatch had four sides, and two swatches were used with each representative culture so that a total of eight trials were reflected with each bacterium. An 8/8 inhibition would indicate 100% efficacy. The test protocol, however, went beyond the specifications of the AOAC method in that the actual average inhibition zone width in millimeters was recorded for both swatches tested. These results were then combined with the anti-microbial spectrum shown in Table 1 which includes the marker bacteria of the AOAC tests, and extrapolated. The conclusion was that the preferred embodiments of the invention were 100% effective against all of the microbes shown in Table 1 and against salmonella based on the previous independent results obtained with silver (I, III) oxide.

Representative results with nylon fabric are shown in Table 2. Generally, the degree of microbial activity varies directly with the silver concentration. In addition to the high performance anti-microbial properties of the fabrics, they withstood wear and could be considered permanent in that tested fabrics withstood 100 hours of laundering and 600 hours of ultraviolet light exposure. Laundering is evaluated using hot water and detergent using the standard test of the American Association of Textile Chemists ("AATC")

Table 2. Antimicrobial Performance of Precipitated Ag_4O_4

Example	Silver (ppm)	Inhibition Zone-SA (mm)	Inhibition Zone-PA (mm)	Inhibition Index
1	89	3.2	1.3	8/8
2	35	1.8	2.0	8/8
3	541	5.5	5.1	8/8
4	3970	5.8	2.6	8/8
5	9140	5.8	2.8	8/8
6	9670	6.1	4.8	8/8

Example 7: Efficacy of Textile Articles of the Invention Against Staph Pathogen

An independent medical researcher in Israel obtained a very virulent strain of Staph from a patient at the Shaarei Tzedek Hospital in Jerusalem. The patient subsequently died from infection. This strain was evaluated as more virulent than any of the other Staph microorganisms listed in Table 1 by the pathology staff at the hospital. This Staph strain was utilized as the Staph source, and the otherwise exact test protocol described above was repeated. The silver concentration of the test swatch was found to be 9,138 PPM. Only one test swatch was used for the Staph evaluation. It tested at 4/4 with a much diminished average inhibition zone of 0.50 mm, which was to be expected for the more virulent strain. The values were extrapolated for all Gram positive bacteria listed in Table 1. It was concluded that precipitated Ag_4O_4 was capable of inhibiting all of the listed Gram positive bacteria. The extrapolation takes into consideration a theoretical calculation of the reduction of the Staph inhibition zone, were the conventional Staph aureus organisms to display the listed MIC range of 2.5 PPM to 5.0 PPM. Since the inhibition zone is inversely proportional to the MIC, one can calculate that the MIC for the virulent Staph strain was 30.5 PPM to 61.0 PPM. By applying the same reasoning to the Gram negative microorganisms for their PA marker, one can claim inhibition as well for all Gram negative bacteria listed in Table 1 by Ag_4O_4.

Example 8: Efficacy of Nylon Articles of the Invention Against Staph Pathogen

Example 1 was repeated with larger amounts of webbing utilizing one foot lengths. Accordingly, webbing was obtained having 4,730 and 9,430 PPM of silver. These materials were dyed orange, and the dye completely covered and hid the brown/black color imparted to the virgin webbing by the tetrasilver tetroxide at these relatively high

concentrations. After dyeing, swatches of the webbing were cut from the master rolls and were then evaluated in the same manner as described above by exposure to Staph aureus. All swatches indicated an 8/8 score, with average inhibition zones of 6.3 and 6.0 for the 4730 and 9430 PPM samples, respectively. Lengths of the dyed webbing were subjected to 100 hours of laundering in accordance with the AATC method, after which bacteriostatic efficacy was again evaluated. Visual inspection after laundering revealed frayed webbing. Nevertheless, both materials exhibited an 8/8 score with an improvement in inhibition zones to 7.0 for Staph aureus. This indicated that the laundry wear tended to expose fresh surface of tetrasilver tetroxide from the fabric interstices. Swatches were again taken from these materials and exposed to 600 hours of ultraviolet light in a weathering test. Evaluations of the UV exposed samples with Staph aureus again indicated scores of 8/8 for both concentrations of silver, with inhibition zones of 6.5 and 4.6, for the 4730 PPM and 9430 PPM silver concentration webbing, respectively. The conclusion was that ultraviolet exposure did not interfere with bacteriostatic activity.

Comparative Example

Monovalent silver iodide was interstitially precipitated within nylon fabric such that the fabric contained 4895 PPM silver. Test swatches were prepared and evaluated against SA and PA pathogens by the test procedure described above. The Inhibition Index for SA was 7/8 and for PA was 0/8. In addition, the SA inhibition zone was only about 0.5 mm.

The following tests were conducted in terms of inhibition of cultures of bacteria. Swatches were used for the tests in contact with the cultures, each swatch having four sides and two swatches being used with each representative culture so that a total of eight trials were reflected with each bacterium. An 8/8 inhibition would indicate 100% efficacy. The test protocol went beyond the specifications of the AOAC methods, however, in that the actual average inhibition zone in millimeters was recorded for both swatches tested. Accordingly, 8/8 positive results were obtained with the marker bacteria cultures. These results were then combined with the anti-microbial spectrum shown in Table 1 which includes the marker bacteria of the AOAC tests, and extrapolated. The conclusion was that the preferred embodiments of the instant invention were 100% effective against the listed Table 1 microbes.

Example 9: Nylon Article Prepared According to the Invention

A swatch of virgin nylon webbing of a standard size, 2.0 mm by 5.0 mm, was taken and immersed for 30 seconds in a cobalt chloride solution containing 10,850 PPM cobalt. A gravimetric determination of the cobalt absorbed after immersion showed cobalt at 9,363 PPM in the webbing. The webbing was then immersed in a room temperature solution containing 50.0 grams/liter potassium persulfate and 22.5 grams/liter sodium hydroxide for two minutes. The webbing was then removed, washed, and dried. The fibers then had a dark brown coating. The swatch was divided into thirds to give three swatches, two for testing in compliance with the AOAC bacterial test 972.04. Zones of inhibition were obtained on all eight sides, *i.e.*, 8/8, for both marker organisms. The average inhibition zones were 1.0 mm for pseudomonas aeruginosa and 1.1 mm for Staph aureus.

Example 10: Nylon Article Prepared According to the Invention

Example 9 was repeated in all aspects except that the solution chemistries were changed and the immersion time in the oxidizer was reduced to one minute. The cobalt as cobalt chloride was 5,400 PPM cobalt and on the fabric was 4,222 PPM. The persulfate oxidizer was identical to Example 9 except that 600 mg/liter of sodium fluoride was added. The results for the Staph marker bacteria were 8/8. The average inhibition zones were 2.0 mm. The addition of fluoride enhanced the efficacy of the fibers against Staph as seen in the inhibition zone being higher than in Example 9 with only 45% of the cobalt concentration that was effective in Example 9.

Example 11: Efficacy of Nylon Article Prepared According to the Invention Against Staph

An independent medical researcher in Israel obtained a very virulent strain of Staph from a patient at the Shaarei Tzedek Hospital in Jerusalem. The patient subsequently died from the infection. This strain was evaluated as more virulent than any of the other Staph micro-organisms listed in Table 1 by the pathology staff at the Jerusalem hospital. This Staph strain was utilized as the Staph source by the researcher who performed the AOAC test 972.04 for bacterial retardation efficacy on the third swatch set aside in Example 9. Since there was only one swatch, there were only four sides to be tested. The virulent strain of Staph was inhibited 100% giving a reading of 4/4. The average inhibition for the 4/4 result was 1.5 mm. Since the virulent strain of Staph qualified on a silver (I, III) oxide scale as having an MIC of 30.5-61 PPM, the values were extrapolated for all Gram positive bacteria listed in Table 1. It was concluded that precipitated cobalt (II, III) oxide was capable of inhibiting all of the listed Gram positive bacteria. By applying the same

reasoning to the Gram negative microorganisms of the Example 9 PA marker, one can claim inhibition as well for all Gram negative bacteria listed in Table 1.

Fabrics treated in accordance with this invention hold promise for many antimicrobial applications ranging from preventing jock itch when applied to athletic supporters to preventing scabies and bed sores with treated bed sheets or hospital gowns used in nursing homes and hospitals.

The invention described and claimed herein is not limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustrations of several aspects of the invention. Indeed, various modifications of the invention in addition to these shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the invention.

CLAIMS

What is claimed is:

1. A fibrous textile article that includes an antimicrobial agent interstitially deposited within the article, the agent comprising a silver (I, III) oxide or a cobalt (II, III) oxide and being present in the article in an amount sufficient to impart antimicrobial properties to the article.

2. The article of claim 1, wherein the antimicrobial agent is interstitially deposited by interstitial precipitation and the antimicrobial properties are sufficient to yield microbial inhibition zones extending beyond 1 mm of fabric swatch borders as measured by AOAC test 972.04.

3. The article of claim 1, wherein the textile article includes woven or non-woven fabric and wherein the antimicrobial agent is present within the fabric at a level in the range of about 0.5 to about 15,000 weight PPM, based on the weight of silver or cobalt.

4. The article of claim 1, wherein the antimicrobial agent comprises a silver (I, III) oxide.

5. The article of claim 1, wherein the antimicrobial agent comprises a cobalt (II, III) oxide.

6. The article of claim 5, further comprising a plurality of fluoride ions.

7. A process for imparting antimicrobial properties to a fibrous textile article, comprising:

providing a first aqueous solution comprising a water-soluble silver or cobalt salt;

contacting the article with the first aqueous solution for a period of time sufficient to uniformly wet the article with the first aqueous solution;

immersing the wetted article in a bath comprising a second aqueous solution comprising a strong alkali and a water soluble oxidizing agent and heating the bath for a period of time sufficient to interstitially precipitate a silver (I, III) oxide or a cobalt (II, III) oxide within the article to yield a finished article; and

removing the finished article from the bath.

8. The process of claim 7, wherein the alkali is sodium hydroxide or potassium hydroxide.

9. The process of claim 7, wherein the oxidizing agent is sodium perfulfate or potassium persulfate.

10. The process of claim 7, wherein the article comprises about 0.5 to 15,000 PPM of the salt, based on the weight of the article.

11. The process of claim 7, wherein the contact of the article with the first aqueous solution comprises immersion of the article in the first aqueous solution for about 15 seconds to about 60 seconds.

12. The process of claim 7, wherein the time of immersion of the article in the second aqueous solution is about 30 seconds to about four minutes. 8. The process of claim 7, wherein the water-soluble silver salt is silver nitrate so that tetrasilver tetroxide is precipitated within the article.

13. The process of claim 7, wherein the water-soluble cobalt salt is cobalt chloride so that a cobalt (II, III) oxide is precipitated within the article.

14. The process of claim 13, wherein the bath further comprises a water-soluble fluoride salt.

15. The process of claim 14, wherein the concentration of fluoride salt in the bath is about 10 to 1500 mg/L.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/00213

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : A01N 25/34, 59/16; A61K 33/24, 33/38
US CL : 424/402, 404, 617, 618; 210/758, 764
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/402, 404, 617, 618; 210/758, 764

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2,791,518 A (STOKES et al.) 07 May 1957, See entire document.	1-15
Y	US 5,211,855 A (ANTELMAN) 18 May 1993, See entire document.	1-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 13 FEBRUARY 2001	Date of mailing of the international search report 16 MAY 2001
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